

Covariance for Conic and Wedge Complete Filling.

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Interfacial phenomena associated with fluid adsorption in two dimensional systems has recently been shown to exhibit hidden symmetries, or covariances, which precisely relate local adsorption properties in different confining geometries. We show that covariance also occurs in three dimensional systems and is likely to be verifiable experimentally and in Ising model simulations studies. Specifically, we study complete wetting in wedge (W) and cone (C) geometries as bulk coexistence is approached and show that the equilibrium mid-point heights satisfy $l_c(h, \alpha) = l_w(\frac{h}{2}, \alpha)$, where h measures the partial pressure and α is the tilt angle. This covariance is valid for both short-ranged and long-ranged intermolecular forces and identifies both leading and next-to-leading order critical exponents and amplitudes in the confining geometries. Connection with capillary condensation-like phenomena is also made.

The central result of density functional theory, which underpins the modern description of inhomogeneous fluids, is that the external potential is a unique functional of the equilibrium density profile $\rho(\mathbf{r})$. That is, $\rho(\mathbf{r})$ is sufficient to completely determine both the range of the surface intermolecular forces and the shape of the confining walls [1, 2].

In spite of this rigorous result, recent studies have highlighted precise connections, or covariances, between adsorption properties for fluids at differently shaped substrates. For instance, the adsorption occurring at wedges and apexes can be related to adsorption properties at a planar substrate in a non-trivial manner [3]. Covariance behaves like a hidden symmetry for fluid interfaces and has a number of profound implications for the theory of wetting, including the allowed values of critical exponents and the very structure of interfacial Hamiltonians [4].

In this paper, we describe a new example of geometrical covariance which relates the interfacial properties of fluids in three dimensional wedges and cones. Unlike previous cases, the covariance we describe here occurs off bulk coexistence, for arbitrary intermolecular forces and in the complete wetting regime, i.e. for zero contact angle. This is of particular relevance since complete wetting is readily accessible in the laboratory [5], implying that the existence of geometrical covariances for fluid interfaces could be verified experimentally for the first time. Indeed, complete wetting in wedges has already been studied in the laboratory with high accuracy [6].

The main result of this paper is the covariance relation

$$l_c(h, \alpha) = l_w\left(\frac{h}{2}, \alpha\right), \quad (1)$$

where $l_w(h, \alpha)$ and $l_c(h, \alpha)$ denote the equilibrium interfacial heights at the mid-point of a wedge and a cone, respectively. Here α represents the substrate tilt angle whilst h measures the partial pressure difference $p_{sat} - p$.

This relation is valid as $h \rightarrow 0$ and describes all diverging contributions to the film thicknesses. We emphasise that similar to other cases of covariance, the above relation exists despite significant differences in the phase transitions occurring in the two geometries.

To begin, we review briefly the basic theory of complete wetting [7]. Consider a planar wall in contact with a bulk vapour at temperature T and chemical potential μ . We suppose that T is above the wetting temperature T_w so that as μ is increased towards saturation $\mu_{sat}(T)$, the thickness of the adsorbed liquid layer l_π diverges, corresponding to zero contact angle $\theta = 0$. The divergence is characterised by the power-law $l_\pi(h) \sim h^{-\beta_s^{co}}$ and is accompanied by the divergence of the transverse correlation length $\xi_{\parallel} \sim h^{-\nu_{\parallel}^{co}}$ and interfacial roughness $\xi_{\perp} \sim h^{-\nu_{\perp}^{co}}$.

The standard way of modelling fluctuation effects at complete wetting is via the effective Hamiltonian [8]

$$H_\pi[l] = \int d\mathbf{x} \left\{ \frac{\Sigma}{2} (\nabla l)^2 + W(l) \right\}, \quad (2)$$

where Σ is the surface tension of the liquid-vapour interface. For systems with long-ranged forces, the binding potential $W(l)$ is given by

$$W(l) = h l + \frac{A}{l^p}, \quad (3)$$

where A is a Hamaker constant and p depends on the range of the forces. For the experimentally relevant case of three dimensions, the cases $p = 2, 3$ correspond to van der Waals (vdW) and retarded vdW forces respectively. In three dimensions, fluctuation effects are not important and a mean-field analysis suffices to determine the critical properties yielding $\beta_s^{co} = 1/(p+1)$, $\nu_{\parallel} = (p+2)/2(p+1)$ and $\xi_{\perp} \sim \sqrt{\ln \xi_{\parallel}}$. In two dimensions, mean-field theory breaks down for $p > 2$ and the exponents are universal

$\beta_s^{co} = \nu_\perp = 1/3$ and $\nu_\parallel = 2/3$ corresponding to the so-called weak fluctuation regime [8].

Now consider the analogous complete wetting in a three dimensional wedge. The wedge is characterised by a tilt angle α so that the height of the substrate above the horizontal (say) is $\psi(x, y) = \tan \alpha |x|$ (see Fig. 1). The wedge geometry enhances the adsorption so that $l_w(h, \alpha)$ is far greater than the thickness of the layer adsorbed at a flat substrate $l_\pi(h)$. The divergence of l_w as $h \rightarrow 0$ is accompanied by the divergence of correlation lengths ξ_x, ξ_y across and along the wedge, and also by the (mid-point) roughness ξ_\perp . However, fluctuation effects are not particularly important at complete wedge wetting and all these length scales can be related to l_w . In particular, $\xi_x \sim \xi_y \sim l_w$ and $\xi_\perp \sim \sqrt{\ln l_w}$. The dominant divergence of l_w follows from simple thermodynamic considerations since the macroscopic meniscus must be an inscribed cylinder with radius Σ/h , as determined by the Laplace pressure [9]. Thus, at leading order, $l_w \approx \Sigma(\sec \alpha - 1)/h$. Similar critical properties occur for the two dimensional wedge although for this case $\xi_\perp \sim \sqrt{l_w}$.

To go beyond the macroscopics and obtain a more accurate expression for l_w , we resort to an effective interfacial Hamiltonian description [10]. This reveals the presence of a significant next-to-leading-order contribution in l_w both in two and three dimensions which itself becomes macroscopic as $h \rightarrow 0$. For convenience, we only present details based on the shallow wedge model,

$$H[l, \psi] = \int d\mathbf{x} \left\{ \frac{\Sigma}{2} (\nabla l)^2 + W(l - \psi) \right\}, \quad (4)$$

appropriate when $\tan \alpha \approx \alpha$. Nevertheless, analysis of a more involved drum-head model results in identical final expressions which are valid for arbitrary tilt angles. Similar to complete wetting at a flat wall, a mean-field analysis suffices to determine the critical properties in three dimensions since both the wedge thickness l_w and the wetting layer thickness l_π are much greater than the roughness. The Euler-Lagrange equation for the relative height $\eta(x) \equiv l(x) - \alpha|x|$ obtained from minimising the Hamiltonian is

$$\Sigma \eta'' = W'(\eta), \quad (5)$$

which is solved subject to the boundary conditions $\eta'(0^+) = -\alpha$ and $\eta'(\infty) = 0$. This equation is integrable and leads to an exact (energy-like) expression for the mid-point height

$$\Sigma \frac{\alpha^2}{2} = W(l_w) - W(l_\pi), \quad (6)$$

where $W(l_\pi)$ is the disjoining pressure for a wetting film. Making use of the Gibbs-Duhem equation $\partial W(l_\pi)/\partial h = l_\pi$ in (6), and reinserting the appropriate geometrical factors for arbitrary tilt angles, we obtain

$$l_w(h, \alpha) \approx \frac{\Sigma (\sec \alpha - 1)}{h} + \sec \alpha D_w l_\pi(h) + \dots, \quad (7)$$

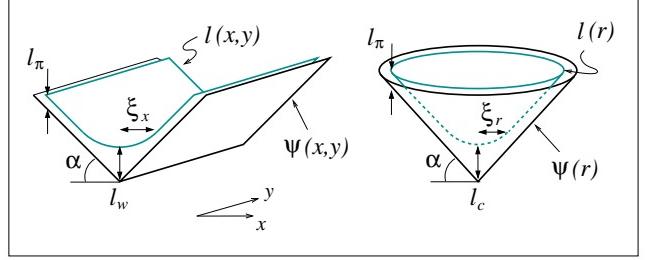


FIG. 1: Schematic diagram of the wedge and cone geometries showing diverging lengthscales.

where the ellipses denote vanishing contributions in the $h \rightarrow 0$ limit, and the critical amplitude D_w takes the non-trivial value

$$D_w = \frac{1}{1 - \beta_s^{co}}. \quad (8)$$

Thus, the next-to-leading-order correction is directly proportional to the planar wetting film thickness and becomes macroscopic in the same limit. The same expansion (7) is also obtained in two dimensions from a transfer-matrix analysis and is valid in both the mean-field and the weak fluctuation regime.

The divergent terms in the interfacial height (7) contribute directly to the divergence of the excess adsorption in the wedge Γ . Thus, for vdW forces, Γ contains leading and next-to-leading-order contributions proportional to h^{-2} and $h^{-4/3}$ respectively. Both these contributions together with their corresponding critical amplitudes have been measured with remarkable accuracy in experimental studies of Ar and Kr on silicon wedges by Mistura and co-workers [6].

It is also instructive to consider the scaling properties of the equilibrium profile. Again, for convenience, we only consider the shallow wedge case, although the results can be readily generalised to more acute systems. From the Euler-Lagrange equation, it follows that $\eta(x) = l_\pi \Lambda_w(x/\xi_x, x/\xi_\parallel)$ where $\xi_x = \Sigma \alpha / h$ is roughly the point of contact of the meniscus with the wall. From this, one sees that the absolute interfacial height $l(x)$ divides into two regions: a filled region for $x < \xi_x$ corresponding to the central meniscus, and a tail for $x > \xi_x$ where the relative interfacial height decays towards its planar value l_π (see Fig. 2). The crossover between the regimes occurs over a distance comparable with the complete wetting transverse correlation length ξ_\parallel . Within the filled region, the meniscus is, to high accuracy, parabolic with

$$l(x) \approx l_w + \frac{h}{2\Sigma} x^2 \quad (9)$$

whilst for $x > \xi_x$ the profile decays exponentially quickly to the planar value

$$l(x) \approx \alpha|x| + l_\pi(1 + Ce^{-(x-\xi_x)/\xi_\parallel}), \quad (10)$$

with C a non-universal constant of order unity. These quantitative features will be of relevance below.

We are now in position to study complete wetting in a cone geometry and establish our main result, the covariance with wedge filling for the mid-point heights. The substrate height is described by the function $\psi(x, y) = \tan \alpha r$, where $r = \sqrt{x^2 + y^2}$ is the radial coordinate (see Fig. 1). As with the wedge, the cone strongly enhances the adsorption compared to the planar wall and the divergence of l_c as $h \rightarrow 0$ is accompanied by the divergence of the radial correlation length $\xi_r \sim l_c$ and mid-point roughness $\xi_\perp \sim \sqrt{\ln l_c}$. Thus, the transition is not fluctuation dominated and can be understood at mean-field level. In the cone, the macroscopic meniscus follows the surface of an inscribed sphere of radius $2\Sigma/h$, since there are two equal radii of curvature contributing to the Laplace pressure. Therefore, the dominant contribution to the mid-point height is $l_c \approx 2\Sigma(\sec \alpha - 1)/h$, twice the value of the corresponding wedge result.

A more microscopic description is afforded by the interfacial Hamiltonian (4) and its drum-head model generalisation. Minimisation of the Hamiltonian leads to the Euler-Lagrange equation for the relative height $\eta(r) \equiv l(r) - \alpha r$,

$$\Sigma \eta'' + \Sigma \frac{\eta' + \alpha}{r} = W'(\eta), \quad (11)$$

which is solved subject to the same boundary conditions $\eta'(0) = -\alpha$ and $\eta'(\infty) = 0$. Unlike the much simpler wedge geometry, this equation is *not* integrable and the analogue of the energy-like equation (6) reads

$$\Sigma \frac{\alpha^2}{2} = W(l_c) - W(l_\pi) + \int_0^\infty dr \frac{\eta'(\eta' + \alpha)}{r}, \quad (12)$$

which is not an explicit expression for l_c . Despite the absence of integrability, one may still obtain the asymptotic divergence of l_c analytically from consideration of the scaling properties of the interfacial profile. We are not aware that analytical results for this system have been presented before. From the Euler-Lagrange equation, we have $\eta(r) = l_\pi \Lambda_c(r/\xi_r, r/\xi_\parallel)$, where $\xi_r = 2\Sigma/\alpha/h$ roughly separates the meniscus region for $r < \xi_r$ from the tail of the profile for $r > \xi_r$. Now, within the small angle approximation, the meniscus is very well described by

$$l(r) \approx l_c + \frac{h}{4\Sigma} r^2, \quad (13)$$

similar to the wedge result (9). The behaviour of the tails, however, is completely different for the cone. For distances $r > \xi_r$, the profile decays algebraically slowly

$$l(r) \approx \alpha r + l_\pi \left(1 - \frac{\xi_r}{2r}\right)^{-\beta_s^{co}}, \quad (14)$$

compared with the exponential decay for the wedge (10). It follows that there exists no rescaling of the bulk ordering field h which maps the *full* cone profile onto the wedge profile.

Incidentally, the presence of the algebraic tails contribute significantly to the adsorption Γ in a cone, somewhat analogous to critical adsorption phenomena. More specifically, in a cone of finite radius R , Γ contains a contribution linear in R arising from the tails in addition to the usual projected area term, that scales as R^2 .

Now focus on the determination of the mid-point conic interfacial height l_c . The energy-like equation (12) for the cone is different to that for the wedge (6) due to the presence of the non-integrable final term, implying that both leading and next-to-leading order contributions to the divergence of $l_c(h)$ which are different to those in l_w , eq. (7). The leading order divergence differs due to a contribution $-\Sigma\alpha^2/2$ in (12) from the integral over the meniscus region $r < \xi_r$. Thus, the leading order divergence of l_c is *twice* that of l_w , consistent with the pure macroscopic considerations above. Similarly, the algebraic tails give rise to a contribution of order $W(l_\pi)$ which alters the next-to-leading order singularity. Carefully making allowance for the full scaling properties of the profile and the specific form of the algebraic tail, it follows, after some algebra, that l_c diverges as

$$l_c(h, \alpha) \approx \frac{2\Sigma(\sec \alpha - 1)}{h} + \sec \alpha D_c l_\pi(h) + \dots, \quad (15)$$

where again the ellipses denote *vanishing* contributions in the $h \rightarrow 0$ limit. The next-to-leading-order correction term is once more proportional to the planar wetting film thickness but has a critical amplitude D_c given by

$$D_c = \frac{2^{\beta_s^{co}}}{1 - \beta_s^{co}}, \quad (16)$$

distinct from the wedge. It is only at this point that the covariance between the interfacial heights for the wedge and cone is manifest. Recalling that the planar wetting film thickness grows as $h^{-\beta_s^{co}}$, it follows that both divergent terms in l_c mimic precisely the wedge expression (7) but at an effective bulk ordering field $h/2$. This leads directly to our central result eq. (1). Numerical results for the mid-point heights obtained from minimisation of Hamiltonian (4) in the wedge and cone geometries are shown in Fig. 2. It can be shown that covariance also applies to the full probability distribution functions

$$P_c(l; h, \alpha) = P_w(l; \frac{h}{2}, \alpha) \quad (17)$$

where, in an obvious notation, $P_c(l; h, \alpha)$ denotes the PDF for the mid-point interfacial height in the cone, etc. By virtue of eq. (9) and (13), the covariance also extends to the shape of the interfacial profiles in the corresponding meniscus regions. All the above statements are valid for small values of h when the mid-point interfacial height is much larger than the planar film thickness.

At this point, we make two remarks:

- Note that the nature of the next-to-leading order correction term in the divergence of $l_w(h)$ and $l_c(h)$ resembles Deryagin's correction to the Kelvin equation for

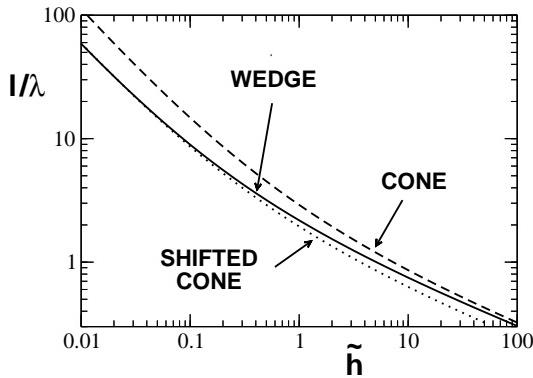


FIG. 2: Graphs of $l_w(h)$ (wedge), $l_c(h)$ (cone) and $l_c(2h)$ (shifted cone) obtained from numerical minimisation of the interfacial model for vdW forces. Dimensionless units, where $A/\lambda^p = \Sigma\alpha^2$ and $\tilde{h} = h\lambda/\Sigma\alpha^2$ are used.

capillary condensation in a slit of width L [11]. In the presence of thick complete wetting layers, condensation is shifted with respect to the bulk and occurs when the width satisfies

$$L \approx \frac{\Sigma}{h} + 2Dl_\pi(h), \quad (18)$$

where Deryagin's amplitude D takes the same value as (8). Only for systems with short-ranged forces, for which $\beta_s^{co} = 0$, do the right-hand sides of (7) and (18) have a direct geometrical interpretation. The similarity is not coincidental and reflects disjoining pressure contributions to the capillary slit, wedge and cone free energies, respectively.

- In addition to experimental studies, the present example of geometrical covariance can also be investigated in Ising model simulations. The reason for this is that, for systems with short-ranged forces, the expression (15) for the divergence of the mid-point height also applies to pyramidal-like geometries where the height-function is $\psi(x, y) = \tan\alpha \max(|x|, |y|)$. Within the simple-cubic Ising model, both wedge [12] and pyramidal-like geo-

metries [13], with $\alpha = \pi/4$, have been used previously to study the critical filling transition occurring at zero bulk field as $\theta \rightarrow \pi/4$. Using the same geometries, but with stronger complete wetting surface fields (so that $\theta = 0$) and off bulk coexistence, one could readily test the effective Hamiltonian prediction of covariance by directly comparing the simulation results for the two geometries.

Finally, as stressed earlier, the covariance between the local interfacial heights at wedge and conic filling does not contradict the central theorem of density functional theory: the confining potential is uniquely determined by the density profile. What covariance implies, however, is that different confining potentials can lead to identical local interfacial properties albeit for rescaled fields. More generally, this implies that quite different examples of interfacial phase transitions share common superuniversal properties. This is perhaps more visible in the previously discussed covariance between 2D critical wedge filling and 2D critical planar wetting. On approaching the critical filling phase boundary, $\theta \rightarrow \alpha$, at bulk coexistence, the mid-point wedge PDF satisfies $P_w(l; \theta, \alpha) = P_\pi(l; \theta - \alpha)$, where $P_\pi(l; \theta)$ is the planar critical wetting PDF written as a function of the contact angle. In these, and other examples of covariance, the relationships between the corresponding interfacial heights in the different geometries only emerges after specific calculations involving both interfacial and more microscopic models. However, the fundamental physical origin of such relations in a more general context remains obscure.

We believe that these different covariances point towards a more comprehensive theorem, perhaps within the framework of density functional theory, that would enable us to further understand the relation between geometry and fluid interfaces.

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